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AUTOMATIC AMS SAMPLE COMBUSTION AND CO₂ COLLECTION

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ABSTRACT. In Groningen, all organic samples for accelerator mass spectrometry (AMS) are combusted in an automatic Elemental Analyzer, coupled to an Isotope Ratio Mass Spectrometer and Cryogenic Trapping System. The Gas Chromatographic (GC) column, part of the Elemental Analyzer system, appeared to be the main cause for memory effects. Therefore we modified the Elemental Analyzer, such that the trapped CO₂ no longer passed the GC column. Our system modification reduced the memory effect significantly, as shown by lower radiocarbon concentration values for anthracite backgrounds, and a much smaller spread in these values. Our modified system can perform up to 40 combustions unattended in about 6 hr.

INTRODUCTION

The Centre for Isotope Research (CIO) of Groningen University has operated a radiocarbon-dedicated accelerator mass spectrometry (AMS) system since 1994. The first results obtained at the Groningen AMS facility were presented at the 15th International Radiocarbon Conference in Glasgow (Gott dang et al. 1995; van der Plicht et al. 1995), followed later by facility reports at the AMS conferences in Tucson, Arizona and Vienna, Germany (Wijma et al. 1997; van der Plicht et al. 2000). For a detailed description of the AMS system, we refer to these earlier reports and to Purser (1992).

For sample preparation, we operate two preparation laboratories with a capacity of about 1000 samples per year each: one conventional, and one AMS. The only obvious difference is the amount of sample material. Organic samples are chemically pretreated to remove contamination before they are combusted to CO₂. The form and intensity of the pretreatment depends on the type, quality and quantity of material. The usual method is acid-alkali-acid (AAA) for charcoal, wood and organic deposits such as peat; Longin for bone collagen extraction; and phosphoric acid for carbonates.

After pretreatment, the organic AMS samples are combusted in an automated Carlo Erba (type NC 2500) Elemental Analyzer (EA). The EA consists of a Cr₂O₃ combustion tube, a silvered cobaltous cobaltic oxide purification furnace, a Cu reduction tube, and a water trap. Such systems are common practice in AMS laboratories (e.g. Aerts-Bijma et al. 1997; Gagnon et al. 2000).

We performed a significant upgrade of the EA setup for automated sample combustion and CO₂ collection. Operational experience taught us that the EA employed the usual (conventional) way is sensitive for sample-to-sample memory effects. This is caused by contamination effects in the GC column. This CO₂ memory effect could be eliminated by a modification of the EA. Here we report on contamination tests for the EA, before and after modification.

Combustion and Graphitization

In original, commercially available EA systems, a Gas Chromatographic (GC) column is used to separate the CO₂ and N₂. The EA can be coupled to a continuous flow Isotope Ratio Mass Spectrometer (IRMS), in our case a Micromass Optima, enabling precise $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements. However, most of the CO₂ is not used for the IRMS, but is “wasted”. For use in ¹⁴C dating, the CO₂ was at first trapped from the waste line cryogenically by hand, and transferred to the graphitization system. Recently, the EA/IRMS system has been expanded with an automatic Cryogenic Trapping

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device (CT). This system consists of 40 separate freeze fingers in a vacuum system. The CT system is described in more detail in (van der Plicht et al. 2000). Each sample, combusted by the EA will deliver its CO₂ (through the waste line) to one of the traps. Each trap has a pneumatic valve and a small cart/elevator with a dewar filled with Liquid Nitrogen can move from trap to trap.

A photograph of the combined EA/IRMS/CT system is shown in Figure 1. The system is fully automated using LabView, under communication with the commercial IRMS software. The total system can combust samples and collect CO₂ unattended for up to 40 samples. It is designed to run over-night. The freeze fingers with the trapped CO₂ are then collected and transferred to the graphitization setup. For graphitization, we employ the method of reduction under Hydrogen excess with Iron powder as catalyst. The graphite is then pressed into a target, which fits into the ion source carousel, using an automatic press (Aerts-Bijma et al. 1997)

The build-up of background, illustrated for various steps during sample handling and based on operational experience, is shown in Figure 2. Backgrounds can increase successively during each step: pretreatment, combustion, graphitization, target pressing, and AMS measurement. A graphite rod



Figure 1 Photograph of the EA/IRMS/CT (from left to right) system, employed for combustion of organic samples for the Groningen AMS facility

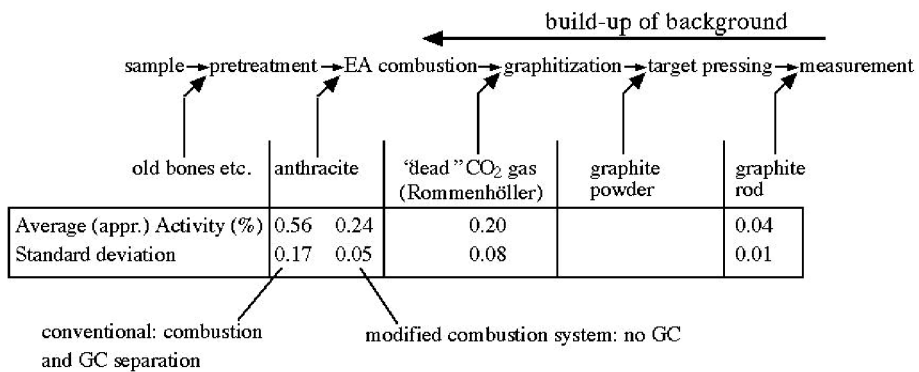


Figure 2 Build-up of background, illustrated for various steps during sample handling

(not subjected to any handling) in the ion source yields ^{14}C background activities of $0.04 \pm 0.01\%$. The background of the graphitization procedure is monitored by Rommenhöller, CO₂ from a natural gas of infinite age. This background activity is $0.20 \pm 0.08\%$. The combustion background is determined by combusting anthracite. The original EA combustion yields background activities of $0.56 \pm 0.17\%$. We found that this can be improved significantly by modifying the EA. This will be discussed in the next chapter.

The EA Modification

In a conventional EA system, the sample is combusted in a hot furnace, yielding CO₂ and N₂ gases after purification and water vapor removal. The complete system is flushed with He gas. The GC column separates the CO₂ from the N₂. After the GC column, a TCD detector measures the amounts of CO₂ and N₂ in the He flow. A small fraction of the EA output (typically 1%) is led to the IRMS in order to measure $\delta^{13}\text{C}$. As explained above, most of the He flow is led through the waste output, and we use this output to cryogenically collect the CO₂ in a liquid nitrogen trap. This EA system (combustion and GC separation) is shown schematically in Figure 3 (top). Such EA/GC/IRMS systems are designed for stable isotope measurements. We call here such systems “conventional”, as opposed to “modified” (described below).

^{14}C analyses, in particular for old samples, are vulnerable for contamination effects. In a conventional EA system as described above, contamination with rest material from previous samples (memory effect) can occur, both in the combustion furnace, and in the GC column. The purpose of the column is the separation of CO₂ and N₂. The commercial EA/IRMS combinations, designed for

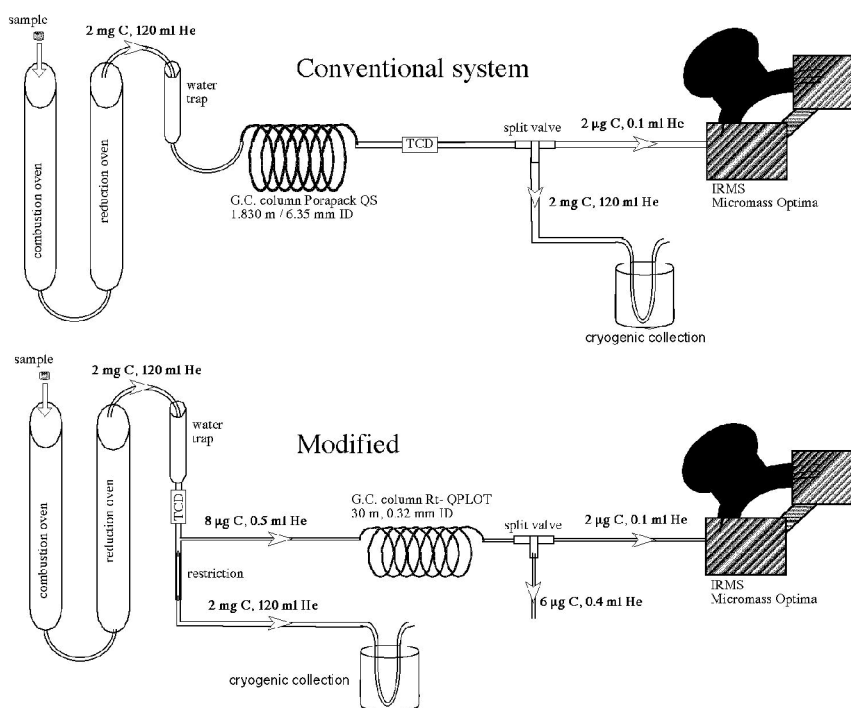


Figure 3 Schematic setup of the elemental analyzer system. Top: conventional (combustion and GC separation); bottom: modified (combustion without GC separation).

stable isotope analysis, deliver typically a few $\mu\text{g C}$ to the IRMS. They are not intended for CO_2 trapping, which is needed for subsequent ^{14}C analysis. Such EA systems, however, are used by many AMS laboratories. Since CO_2 trapping is done cryogenically, the GC column is in fact superfluous since the Liquid Nitrogen trap separates the CO_2 in the He-flow from other gases such as N_2 , and possibly traces of O_2 . Therefore, we modified the EA/IRMS design as shown in Figure 3 (bottom). The gas flow through the system (CO_2 after combustion and He carrier gas) is 120 mL/min with 2 mg C. The flow is split in 2 pathways: 1) 119.5 mL/min He ("waste") with about 2 mg C to the CT system, and 2) 0.5 mL/min He with about 8 $\mu\text{g C}$ to a different type of GC column (see Figure 3 for column types) followed by a splitter valve. The latter reduces the flow to the IRMS to the desired 0.1 mL/min ($\sim 2 \mu\text{g C}$), whereas its waste line contains the remaining waste. In this configuration, the bulk of the CO_2 (corresponding to about 2 mg C) flows directly from the combustion/purification ovens into the cryogenic trapping system, without being affected by the GC column. Only the small fraction needed for the IRMS ($\sim 10 \mu\text{g C}$), is GC-separated by a small column.

RESULTS AND DISCUSSION

We have performed contamination tests by ^{14}C analysis of ANU-sucrose and anthracite, by means of alternating combustion in our EA/IRMS/CT system. This was done for both the conventional EA system, and for the modified EA system. The ^{14}C activity of ANU-sucrose is 150.6% (Rozanski et al. 1992) whereas anthracite is the commonly used material for background determination. The sample size was 2 mg C in all cases. After combustion and trapping, the CO_2 was transported to the graphite system. Next, the graphite was pressed into sample holders for the AMS ion source (Aerts-Bijma et al. 1997), and finally the ^{14}C content was measured by the AMS.

The results of the contamination tests are shown in Figure 4. The conventional and modified EA systems were used in parallel, using the same IRMS and the same CT system. Figure 4 (top) shows the AMS- ^{14}C results for alternating combustion of, at first, ANU-sucrose, followed by two combustions of anthracite. The anthracites for the conventional system (squares) show significant memory effects. For our modified system (circles), no memory effects are visible. From the comparison of the two, it is clear that in the conventional system, even the second anthracite sample in row still suffers from significant traces of the sucrose sample, present in the GC column.

Combustion of blank samples (empty tin cups commonly used for the EA) in between all samples, for reasons of cleaning the combustion furnace, does not lead to improvement for the anthracite results using the conventional EA setup (Figure 4, bottom).

Apparently, the traces of CO_2 from the previous sample in the GC column cannot be washed out by the flow; they can only be diluted by a new burst of CO_2 . The modified system does not show further improvement by the blank combustion either, which indicates that memory effects due to remains in the combustion oven are negligible.

Comparison of the behavior of the conventional and modified EA setup (Figure 4) shows that in the conventional setup, about 0.4% of the previous sample is admixed to the next one. This explains the average value of 0.57% for anthracite samples in the conventional setup, as well as its relatively large spread of 0.17%.

In the modified system, the average value for anthracite is $0.24 \pm 0.05\%$. This value overlaps with the Rommenhöller gas background value for the graphitization system (see Figure 2), from which we conclude that the memory effect of our modified system is now negligible. Especially the large

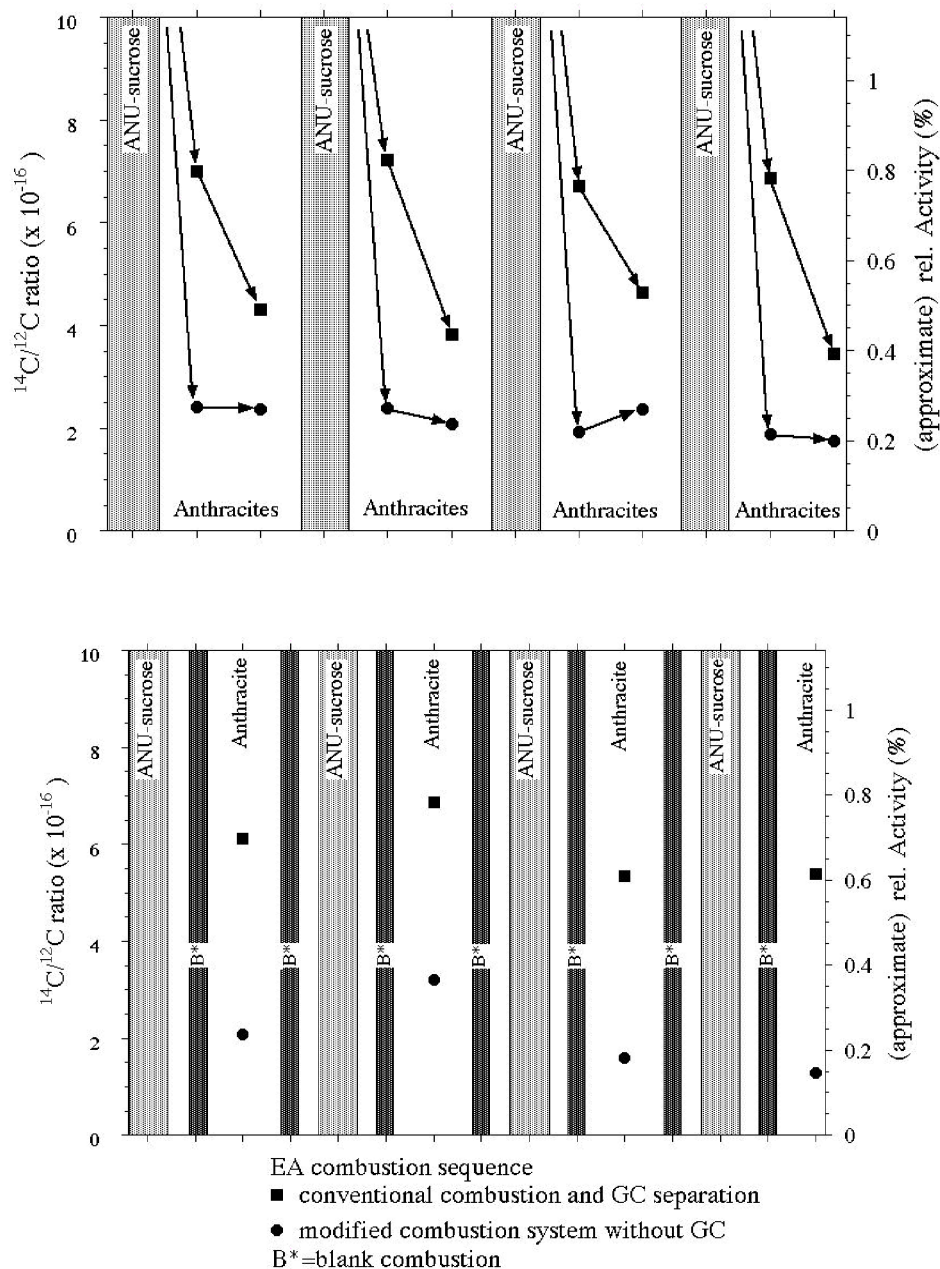


Figure 4 (top and bottom) Results for alternate combustions of ANU-sucrose and anthracite showing contamination effects for both the conventional and the modified EA setup. Left scale: $^{14}\text{C}/^{12}\text{C}$ ratio; right scale: (approximate) ^{14}C activity in %. Top: alternating combustion of sucrose and then two anthracite samples; bottom: alternating combustion of sucrose, blank and anthracite samples.

reduction of the spread in the background values from conventional to modified system has improved the accuracy of dating older samples in our laboratory.

Since we do not any longer employ CO₂ separation by the GC column, we might be more sensitive to impurity of the gas. The purity, however, is maintained because halogens and SO₂ are removed by the silvered cobaltous cobaltic oxide in the oxidation tube.

We realize that EA column behavior depends on column age and treatment, and that it might be possible to reduce the memory effect by column treatment or replacement. However, for ¹⁴C use it will always be a part of concern, and in our modified system we have solved this problem radically.

Our modified EA/IRMS/CT combination combusts and collects automatically up to 40 samples, unattended, in a period of about 6 hr.

CONCLUSIONS

We have shown that in conventionally used elemental analyzers, where the GC column is used to separate the CO₂, this column is a main cause of sample-to-sample memory effects. This memory effect hardly decreases after a blank (no sample), even after extra anthracite combustion it has not vanished. Our modified design, based on CO₂ isolation using cryogenic trapping, eliminates this memory effect. For ¹⁴C analysis, this leads to significantly lower background activities. In addition, the spread in the background activities is much lower, enabling a better and more accurate background correction for samples. The modification is easy to perform and cheap.

We have shown that the conventional EA yields backgrounds activities of $0.56 \pm 0.17\%$; after modification, this background activity becomes $0.24 \pm 0.05\%$.

In the modified version, the EA setup no longer contributes to the build-up of sample contamination. At present, our graphitization system is likely to be our most important remaining source of contamination. A planned upgrade of the EA/IRMS/CT system is an online graphitization setup, avoiding transporting CO₂ from one location to the other.

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